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Phase Diagrams of Binary Nematic Mesophase Systems†

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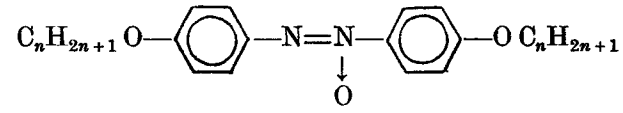
Abstract—Temperatures and heats of transition are presented for four binary nematic mesophases; *p*-azoxyanisole plus *p*-azoxyphenetole, *p*, *p*′-*n*-dipropoxyazoxybenzene, *p*,*p*′-*n*-dibutoxyazoxybenzene and *p*,*p*′-*n*-dihexyloxyazoxybenzene. The phase diagrams were shown to be of the simple eutectic type with the formation of ideal comesophase solutions permitting prediction of the eutectic composition and temperature. The heats of transitions can be estimated with reasonable accuracy.

Introduction

Extensive studies of temperatures and heats of transitions, specific heats and entropies have been reported for individual mesophase or liquid crystal compounds (see for example Ref. 1). Relatively few reports of similar studies on binary mesophase systems have appeared. For binary nematic systems transition temperatures have been reported by Prins,[2] Dave and Dewar,[3] Dewar, Schroeder and Schroeder,[4] Arnold and Sackmann[5] and Dehl and Steinstraesser.[6] This work reports both temperatures and heats of transitions and entropies for four binary nematic systems.

Experimental

The compounds studied were of the type



† Part XXXIV of a series on " Order and Flow in Mesophases ".

and were *p*-azoxyanisole (PAA $n=1$), *p*-azoxyphenetole (PAP $n=2$), *p,p'-n*-dipropoxyazoxybenzene (DPAB $n=3$), *p,p'-n*-dibutoxyazoxybenzene (DBAB $n=4$), and *p,p'-n*-dihexyloxyazoxybenzene (DHAB $n=6$). All compounds were obtained from Eastman Organic Chemicals (Rochester, New York).

Initial purification was by recrystallization from absolute ethanol repeated three times. Purities were determined using a Perkin–Elmer DSC-1B as previously described.[7,8] A second purification step was made by use of a Fisher zone refiner. Approximately 30 passes were used. In every case a significant increase in purity was observed. Purities, transition temperatures and heats of transitions are reported in Table 1.

Phase transition temperatures were measured using a Dupont Model 900 Differential Thermal Analyzer equipped with DSC cell and a nitrogen atmosphere. The temperature axis of the instrument was calibrated with the known melting points of benzoic acid (121.2 °C) and indium (156.6 °C). The heating rate in this investigation was 5 °C/min. Duplicate runs of each sample showed no shift in the vertex of the endothermal minimums.

The heats of transition were determined independently by differential scanning calorimetry using the Perkin–Elmer DSC-1B instrument operated at scanning rate of 10, 5 or 1.25 °C/min on heating. The apparatus was calibrated by measuring the known heat of fusion for benzoic acid (33.9 cal/gm) and indium (6.80 cal/gm). The techniques of sample containment and calculation were essentially the same as those described elsewhere.[9]

The samples were weighed into small pyrex test tubes and sealed under nitrogen. The contents of the tubes were melted at about 10 °C above the highest transition temperature and mixed thoroughly. This procedure was then repeated to insure homogeneity.

Results and Discussion

Typical thermograms for pure nematic compounds and a mixture are shown in Fig. 1. Typically three endothermal transitions were observed for binary mixtures. In order of increasing transition temperatures these are: (a) transition from the crystalline solid mixture to two phases, the nematic mesophase and excess pure

TABLE 1 Thermodynamic Data of Five Nematic Compounds (Solvent recrystallized and zone refined)

Compound	Symbol	Purity mole %	Transition temperatures and transition heats: Solid → Nematic T °C	Solid → Nematic ΔH cal/gm	Nematic → Isotropic T °C	Nematic → Isotropic ΔH cal/gm
p-Azoxyanisole	PAA	99.98	119.5	28.0	136.5	0.65
p-Azoxydiphenetole	PAP	99.96	137.8	22.9	167.8	1.77
p,p'-n-Dipropoxyazoxybenzene	DPAB	99.49	118.3	20.5	124.0	0.88
p,p'-n-Dibutoxyazoxybenzene	DBAB	99.83	105.8	14.6	136.6	1.21
p,p'-n-Dihexyloxyazoxybenzene	DHAB	99.57	79.6	24.3	127.7	1.23

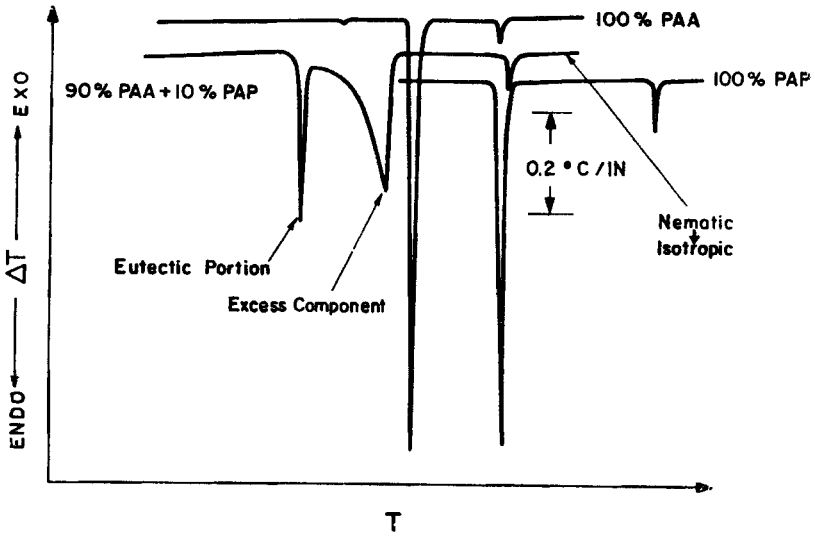


Figure 1. Typical Thermograms of Pure and Binary Mesophase Systems.

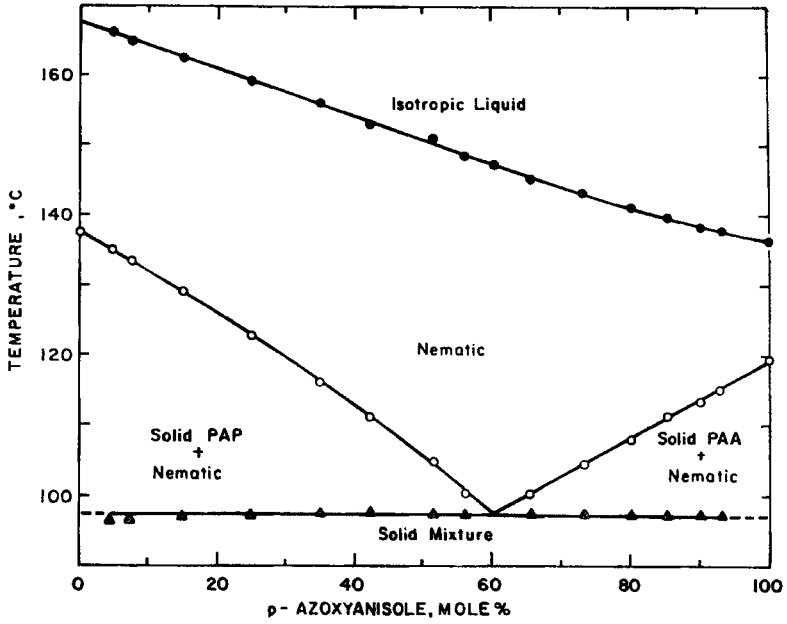


Figure 2. Phase Diagram of *p*-Azoxyanisole-*p*-Azoxyphenetole System.

crystalline solid, (b) transition from the two phase region to a one phase region in which the two components were completely miscible which has been referred to as " nematic comesophase " and (c) transition of the nematic mesophase to an isotropic liquid where again both compounds are completely miscible.

Figures 2 through 5 show the four binary phase diagrams. In each case a eutectic composition exists where only two transitions are observed. At the eutectic the transitions are from the solid mixture to the nematic comesophase to the isotropic liquid. Results have been previously reported for the temperature of transition and eutectic compositions for the systems PAA–PAP and PAA–DHAB. These are included with the results of this work in Table 2. In general the results are in good agreement.

All phase diagrams were of the " simple-eutectic " type. The area below the eutectic temperature, T_e, consisted of a mechanical mixture of the two terminal solid solutions which probably contain only a small amount of the second component. The composition of the terminal solid solutions apparently have approximately 5% or less of the minor component.

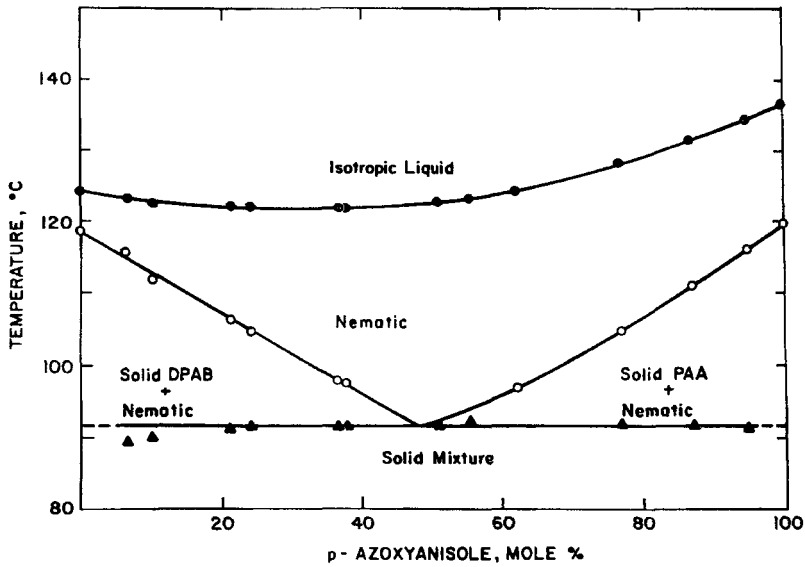


Figure 3. Phase Diagram of p-Azoxyanisole-p,p'-n-Dipropoxyazoxybenzene System.

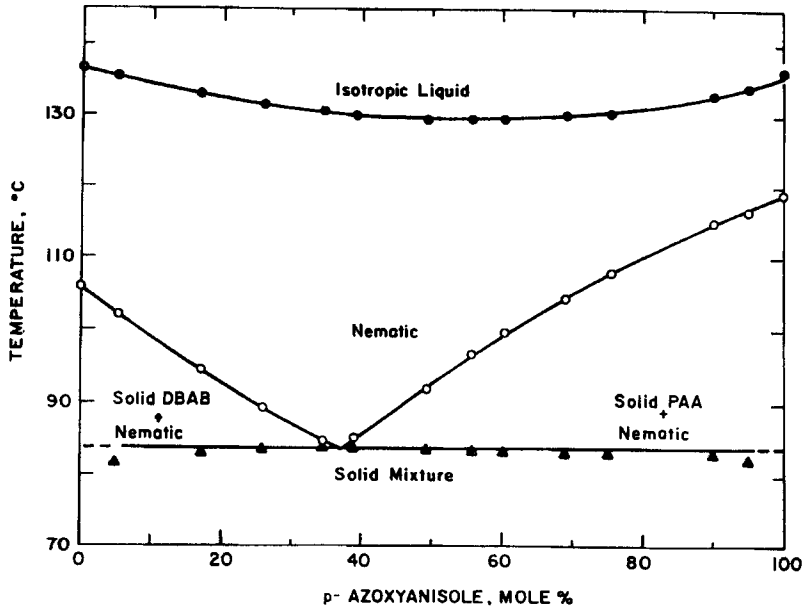


Figure 4. Phase Diagram of *p*-Azoxyanisole-*p*,*p*′-*n*-Dibutoxyazoxybenzene System.

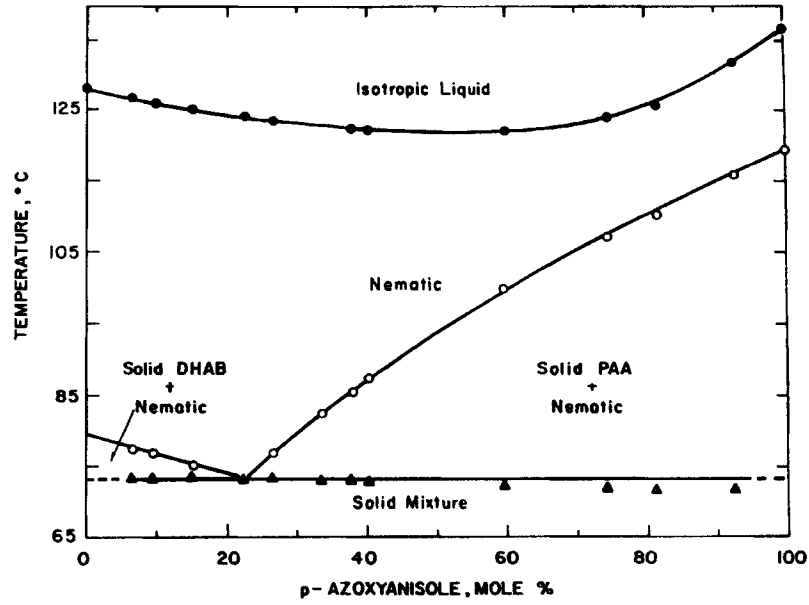


Figure 5. Phase Diagram of *p*-Azoxyanisole-*p*,*p*′-*n*-Dihexyloxyazoxybenzene System.

TABLE 2 Calculated and Measured Eutectic Temperatures and Compositions

System	Eutectic temperature, °C		Eutectic composition mole% PAA		Eutectic formula	Nematic range, °C (at the eutectic point)	Reference
	Calculated	Measured	Calculated	Measured			
PAA–PAP	96.6	97.4	59	60	A_3B_2	50	This work
		97.0		62			(2)
		97.0		61			(5)
		97.5		60			(10)
PAA–DPAB	90.0	92.2	49	48	A_1C_1	31	This work
PAA–DBAB	80.5	83.5	38	37	A_2D_3	49	This work
PAA–DHAB	71.5	73.2	26	24	A_1F_3	50	This work
		77.0		27			(4)

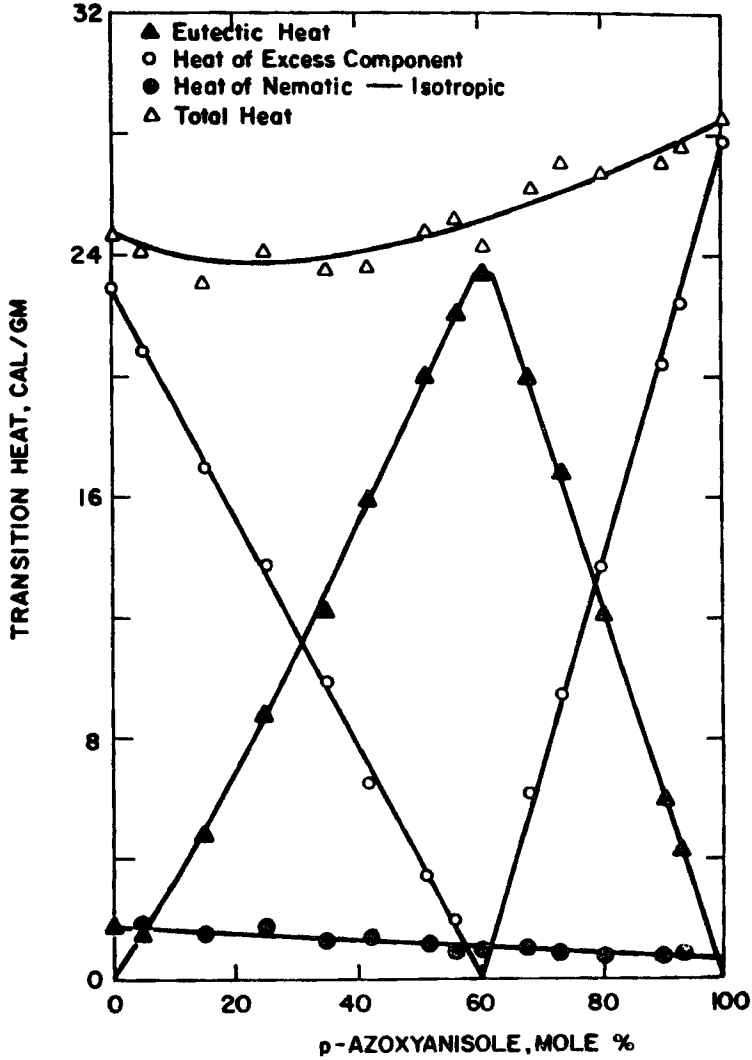


Figure 6. Transition Heats of *p*-Azoxyanisole-*p*-Azoxyphenetole System.

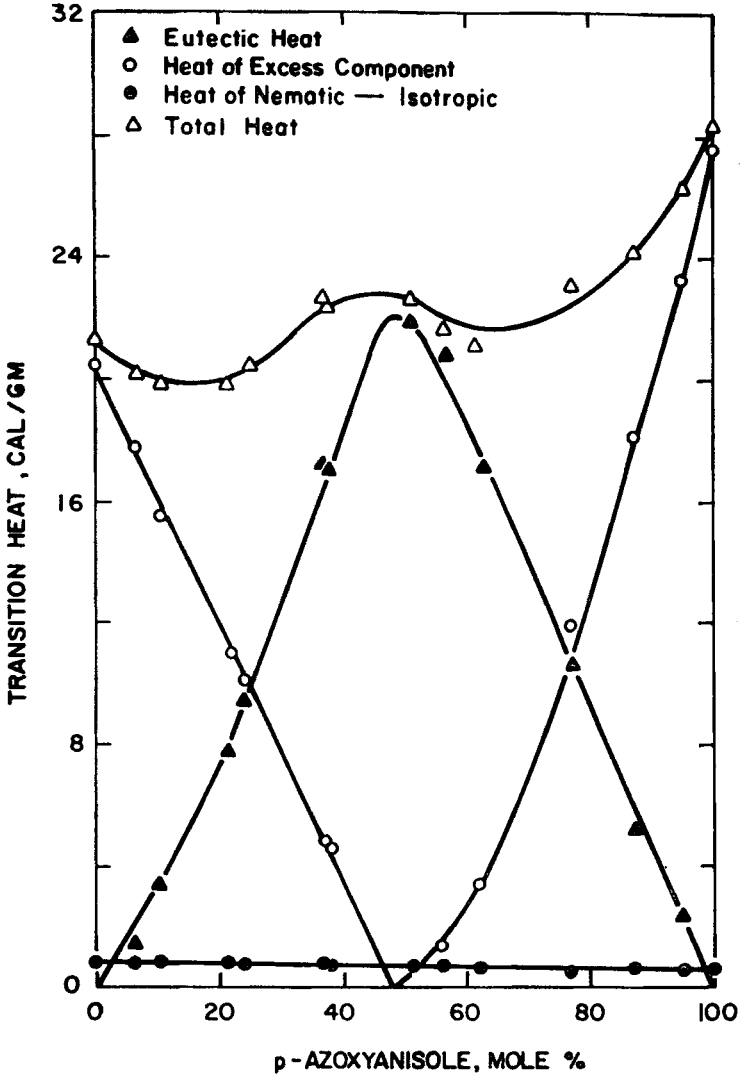


Figure 7. Transition Heats of *p*-Azoxyanisole-*p*,*p*′-*n*-Dipropoxyazoxybenzene System.

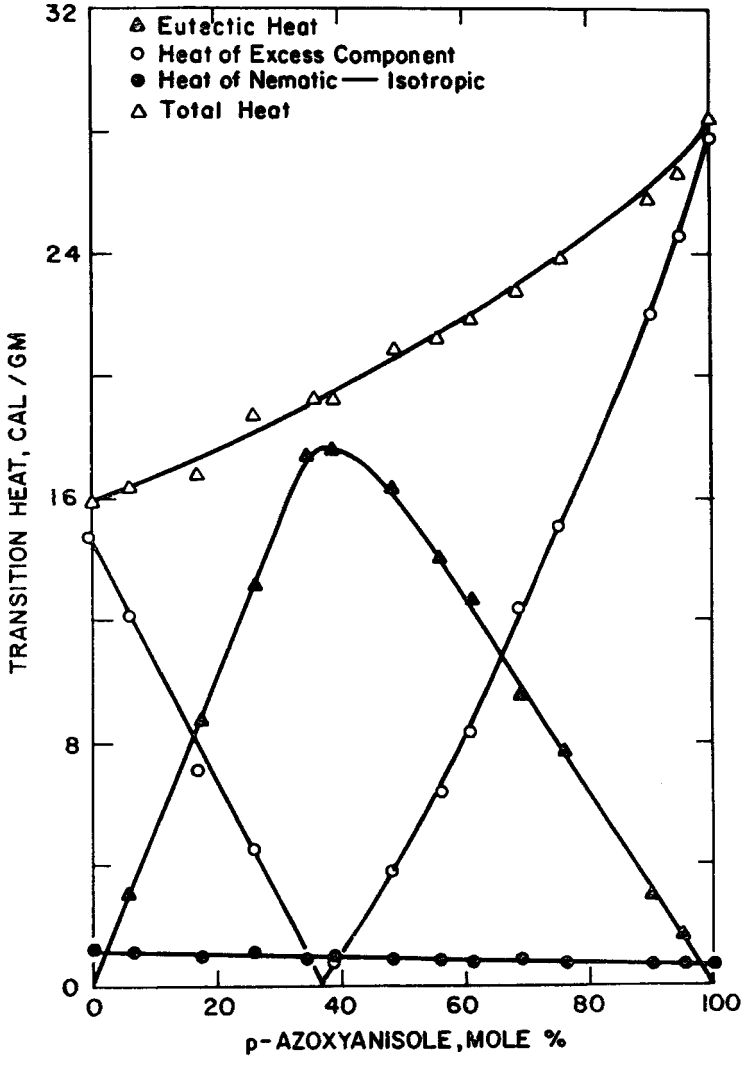


Figure 8. Transition Heats of *p*-Azoxyanisole-*p,p'*-*n*-Dibutoxyazoxybenzene System.

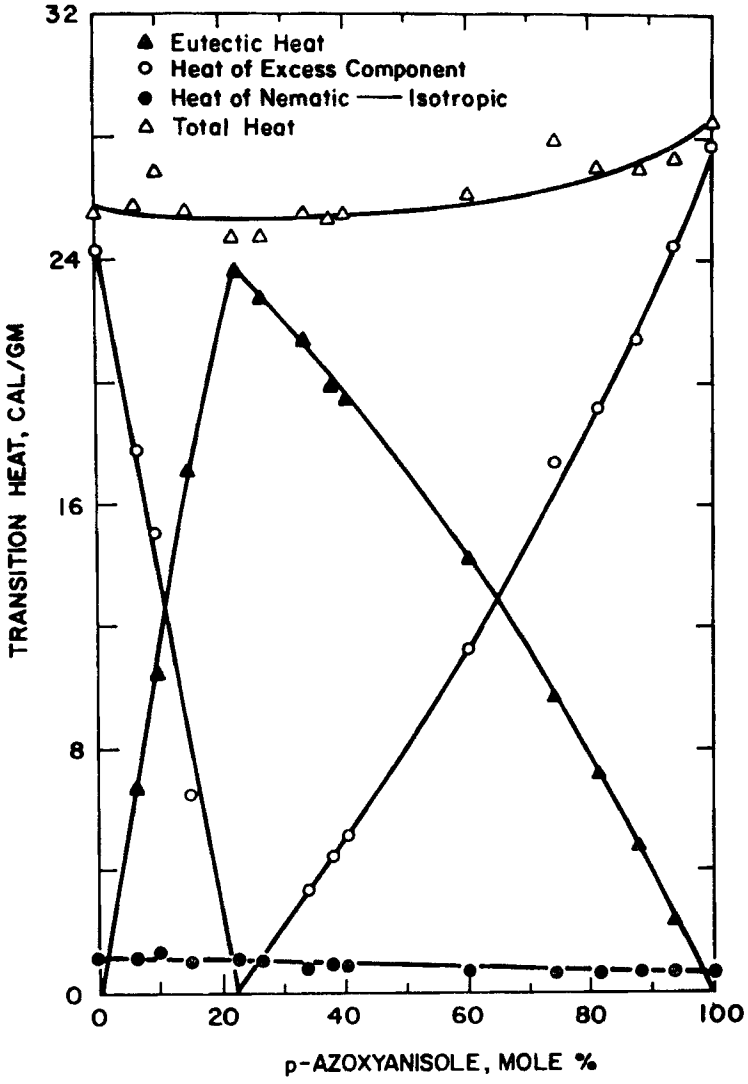


Figure 9. Transition Heats of *p*-Azoxyanisole-*p,p'*-*n*-Dihexyloxyazoxybenzene System.

Above the eutectic temperature and below the liquidus curves there are two phase regions with solid crystalline material in equilibrium with the nematic mesophase. Above the liquidus curves a single nematic comesophase exists until the transition temperature to the isotropic liquid is reached.

The nature of the nematic comesophase can be examined by use of the Schröder–van Laar equations.

$$-\ln X_1 = \frac{\Delta H_{f1}}{R}\left(\frac{1}{T} - \frac{1}{T_1}\right)$$

$$-\ln (1 - X_1) = \frac{\Delta H_{f2}}{R}\left(\frac{1}{T} - \frac{1}{T_2}\right)$$

where ΔH_{f1}, T_1 and ΔH_{f2}, T_2 are the heats of fusion and transition temperatures of pure components 1 and 2 from the crystalline solid to the nematic mesophase, T is the transition temperature for a two component system containing X_1 mole fraction of component 1, and R the gas constant. Simultaneous solution of the two equations permits calculation of the eutectic temperature and composition. A comparison of calculated and measured results is given in Table 2 and shows excellent agreement. This demonstrates that each of the systems forms ideal solutions over the entire composition range. Formation of ideal solutions is reasonable in view of the similar structures of the components and the small differences between the heat capacities of the crystalline solids and mesophases.[11,12]

Figures 6 through 9 show the transition heats for the binary systems. For each of the four systems the following behavior is observed:

(a) The heat of transition of the nematic comesophase to isotropic liquid varied only slightly between any two pairs and the various compositions gave values that fell approximately on a line connecting the two values.

(b) The eutectic heat of transition increases approximately linearly with the concentration of the second component in either pure component until a maximum is reached at the eutectic composition. When the experimental data is fitted to a straight line by the least squares method, the plot can give some idea about the limit of solid solubility. The results obtained by this method were as follows:

A B	Limit of Solid Solubility, Mole % B in A	A in B
PAA–PAP	0.6	2.8
PAA–DPAB	0.0	4.6
PAA–DBAB	−0.8	−2.0
PAA–DHAB	−4.9	0.3

The precision of the method is not sufficient to justify any quantitative conclusions as evidenced by the negative numbers. It is reasonable to conclude that the limit of solubility is probably 5% or less.

(c) The heat of transition of the excess component decreases approximately linearly with the concentration of the second component in either pure component until a minimum value of zero is reached at the eutectic composition.

(d) The value of the total heat in three of the systems falls on a line that is slightly concave upwards between the two components. In the fourth case more irregular behavior is observed. Entropy plots show very similar behavior to Figures 6 through 9 as expected.

In every case the eutectic composition gives the nematic comeosophase behavior over the widest temperature range. For binary nematic mesophases of similar composition it is reasonable to assume ideal behavior. Thus the temperature phase diagrams can be predicted with good accuracy. The heats of transition phase diagrams can be estimated with reasonable precision as outlined in (a) through (d) above.

Acknowledgement

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